Conductivity of Thionyl Chloride-Lithium Tetrachloroaluminate Solutions

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Conclusion

The cathode performance in the solid electrolyte cells containing manganese dioxide depends on two factors. One is the macroscopic factor, *i.e.*, the uniformity of dispersion or the degree of distribution of manganese dioxide in the cathode mixture. The degree of distribution of the components is related to the grain shape, average grain size, grain size distribution, density, and specific volume. If the mixing of the component powders is well done, the operative contact area will be achieved appropriately. The distribution of the cathode components was achieved in the CMD-C-X system more uniformly than in the EMD-C-X system.

The other subject on manganese dioxide is the microscopic factor with regard to the crystal structure, adsorbed and structural water, surface area, average pore volume, and average pore diameter. However, differing from the liquid-type batteries, the surface area, pore volume, and pore diameter appear not to influence the cathode performance of the solid state cells so much. The thermal treatment of the EMD indicated that the grain of higher crystallinity was superior to the grain of lower crystallinity and that the γ phase was better than the β phase.

The discharge performance of the solid electrolyte cell with the CMD was better than that of the cell with the EMD. The discharge mechanism of the manganese dioxide cathode is regarded as similar to the discharge mechanism in Leclanché dry cells. The discharge reaction or the electrochemical reduction of manganese dioxide in the mixed-phase cathode is a one-phase reaction, and the mechanism is the double injection of copper (I) ions and electrons into the lattice of manganese dioxide. In this study, the rechargeability of the solid electrolyte cells was briefly tested to reveal rather low reversibility of the copper (I) ion intercalation into and from manganese dioxide. The study on the rechargeable cells with oxide cathodes is in progress.

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Conductivity of Thionyl Chloride-Lithium Tetrachloroaluminate Solutions

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ABSTRACT

The specific conductivity of solutions of $LiAlCl_4$ dissolved in $SOCl_2$ was determined as a function of composition and temperature. An analytical expression from which the conductivity can be calculated is given as a function of the mole fraction of $LiAlCl_4$ and temperature in the ranges from 0° to 0.37°C and from −20° to +70°C, respectively.

$LiAlCl_4$-$SOCl_4$ mixtures are used commercially as electrolytes in lithium batteries (1).

Thionyl chloride itself has a low melting point (−104.5°C), a low vapor pressure (*ca.* 15 kPa at 25°C), a high boiling point (77°C), but a low electrical conductivity (*ca.* $3.5 \cdot 10^{-9}$ S cm^{-1} at room temperature). To be useful in a battery, salts must be dissolved in the $SOCl_2$. One common choice of such a salt with a large solubility in thionyl chloride is $LiAlCl_4$. However, the conductivities of these solutions are only approximately known (1-8).

We decided to check and extend the available conductivity data. Apparently at all temperatures studied in the literature there is an optimum concentration of $LiAlCl_4$ for maximum conductivity.

During the present work we found the position of this maximum conductivity and derived an analytical expression from which the specific conductivity of any $LiAlCl_4$-$SOCl_2$ solution can be calculated with a high degree of precision.

The high conductivity of $LiAlCl_4$-$SOCl_2$ solutions compared with other lithium inorganic room temperature electrolytes was pointed out by Auborn and co-workers (2), who reported among other things the conductivity as a function of concentration of $LiAlCl_4$ in $SOCl_2$ up to 2.0*M* at 25°C. They found that a maximum conductivity of 0.0204 S cm^{-1} was reached in *ca.* 1.7*M* solution. Very dilute solu-

* Electrochemical Society Active Member.

tions of $LiAlCl_4$ in $SOCl_2$ have also been studied by others (3).

The combined temperature and concentration dependences of the conductivity, density, and viscosity were studied extensively by Venkatasetty and Szpak (5-7). In these works, conductivities are reported as a function of concentration.

Because of volume changes, concentration itself is a function of temperature. This function has only been reported indirectly in density *vs.* temperature relations at certain concentrations. In our estimation this is not adequate. Either a solution must be prepared at the temperature in question or a correction procedure is required. This procedure, involving knowledge of concentration changes cannot be easily performed because the previous authors (5-7) have not supplied the data required nor described exactly how they obtained their corrected concentrations. Without corrections, only limited accuracies can be attained. To allow for high precision and simple calculations we derived an analytical expression based on mole fraction and temperature as independent parameters.

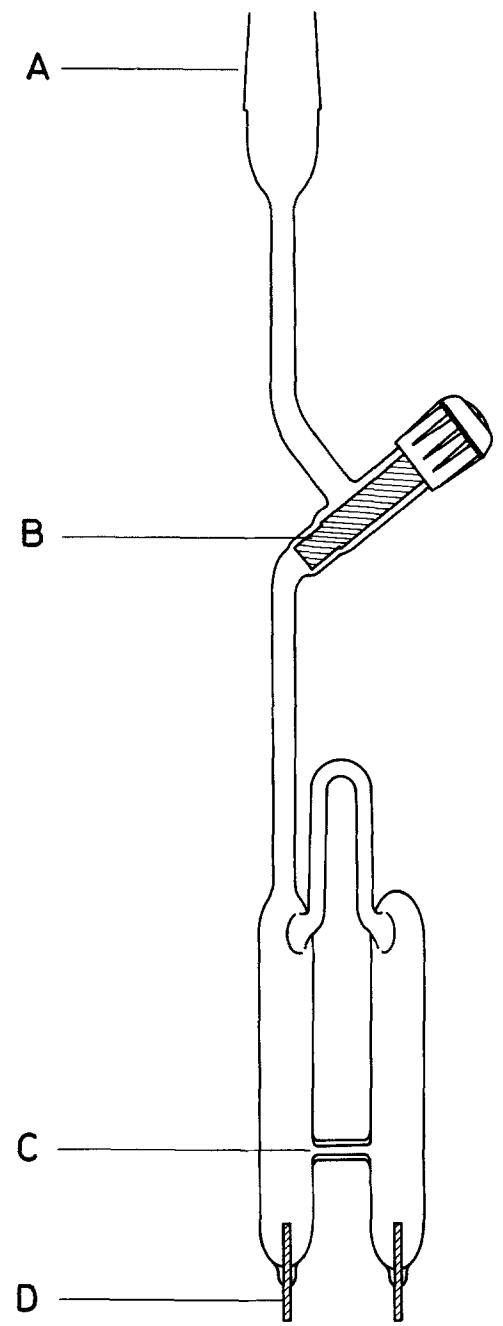

Fig. 1. Conductivity cell made of Pyrex glass: (A) conical joint, (B) Teflon stopcock, (C) capillary tube (0.1 mm$^\phi$ · 20 mm) between cell compartments, (D) vitreous carbon electrode (3 mm$^\phi$, from Carbone-Loraine, baked and sealed into the glass).

Experimental

Because of the moisture sensitivity of the chemicals, all manipulations involving compounds were carried out in a glove box with dry air atmosphere (dew point <-45°C). Conductivity cells were only taken out of the glove box after being securely closed.

Chemicals.—Thionyl chloride from Fluka (puriss. $SO_2Cl_2 < 0.03\%$; $SCl_2 < 0.03\%$) was refluxed (in the glove box) for several hours in contact with cleaned, granulated lithium metal of the highest available purity. During this cleaning operation, the conductivity of $SOCl_2$ at 25°C dropped from $141 \cdot 10^{-9}$ to $43 \cdot 10^{-9}$ S cm^{-1} and the liquid became faintly yellow, presumably due to traces of sulfur containing compounds. By subsequent distillation over fresh P_2O_5 and discarding the first yellow fraction (50% of total), it was possible to obtain a small amount of $SOCl_2$ distillate having no color and a room temperature conductivity of $11.3 \cdot 10^{-9}$ S cm^{-1}. In the $LiAlCl_4$-$SOCl_2$ experiments reported here, only the refluxed $SOCl_2$ was used because the amount of charge carrying impurities already in this first batch was insignificant in comparison with the added solutes.

Lithium tetrachloroaluminate was made by mixing (at 175°C over night in a rocking furnace) equimolar amounts of LiCl and $AlCl_3$ in a cell sealed under vacuum. LiCl (pro analysis from Riedel-de Haen) was purified in the molten state in a quartz apparatus by flushing with dry, pure HCl gas, by filtering and then by recrystallization in an N_2 gas atmosphere. Titration of Cl^- by the Volhard method showed no significant deviation from the theoretical Cl-content. $AlCl_3$, anhydrous, p.a. was obtained from Fluka and distilled several times in sealed cells, as described elsewhere (9).

Conductivity cells.—Four conductivity cells, A-D, made from Pyrex glass in a manner as described in detail in Ref. (10) (depicted in Fig. 1) were used for the determinations. Cell constants (of the order 100-400 cm^{-1}) were determined at 25.0°C by the standard method (11) using 0.1000 Demal aqueous KCl solutions made by weight from analyzed dry KCl and distilled water. Corrections for temperature expansion of the Pyrex cell was omitted since it never exceeded 0.03%. Weighed amounts of $LiAlCl_4$ were transferred to rinsed and dried cells. Thionyl chloride was then added by means of a calibrated pipette. Experimental details are given in Table I. In some experiments further chemicals were added to the cells (in the glove box) by opening stopcocks and introducing specified amounts of materials and of $AlCl_3$.

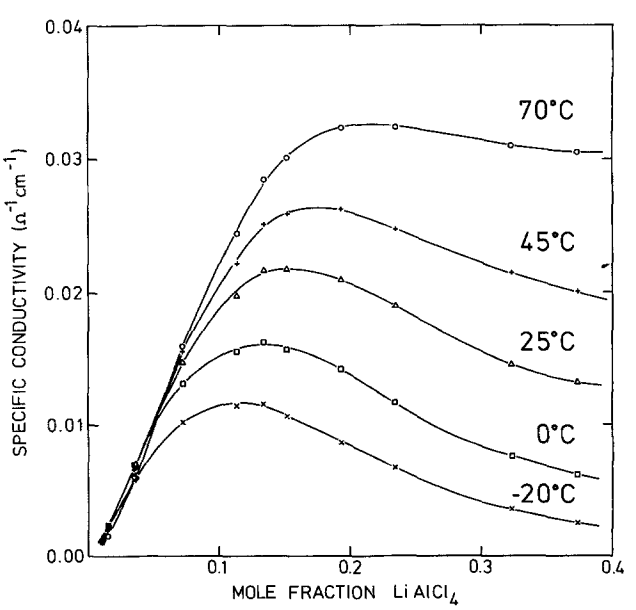

Fig. 2. Specific conductivity (κ) of $LiAlCl_4$-$SOCl_2$ solutions *vs.* mole fraction *X* of $LiAlCl_4$ at different temperatures. (κ, *X*) data were interpolated as explained in the text and are connected by smooth curves.

Table I. Experimental details for conductivity experiments

Cell[a]	Experiment[b]	$LiAlCl_4$[c] weight (g) ± 0.001	$SOCl_2$ volume (cm^3) ± 0.05	X_{LiAlCl_4}[d]	$AlCl_3$ weight (g) (± 0.001)	X'_{AlCl_3}	Approximate density[e] at 25°C	Approximate concentration[e] of $LiAlCl_4$ at 25°C (mol/liter)
A	1	0.883	10.00	0.0354	—	0.500	1.665	0.485
A	2	2.158	5.00	0.1520	—	0.500	1.734	2.08
A	2*	4.026	7.00	0.1929	—	0.500	1.76	2.64
A	3	5.740	4.00	0.3735	—	0.500	1.87	5.1
A	4	0.450	5.00	0.0361	—	0.500	1.665	0.495
B	1	0.938	5.00	0.0723	—	0.500	1.687	0.991
B	1*	2.159	7.00	0.1136	—	0.500	1.711	1.556
B	2	2.946	4.00	0.2343	—	0.500	1.78	3.2
B	2*	5.746	5.00	0.3232	—	0.500	1.84	4.4
B	3	0.186	5.00	0.0152	—	0.500	1.653	0.21
C	1	3.718	10.00	0.1338	—	0.500	1.72	1.83
C	1*	3.718	10.00	—	0.055	0.505	1.72	1.8
C	1**	3.718	10.00	—	0.482	0.539	1.72	1.8
D	1	1.031	11.00	~0.0375	~0.004	0.501	1.67	0.51
D	1*	1.031	11.00	—	0.025	0.508	1.67	0.5
D	1**	1.031	11.00	—	0.143	0.542	1.67	0.5

[a]The cell constants of the four cells were $A = 345.4$, $B = 113.3$, $C = 226.9$, and $D = 211.9$ cm^{-1}.
[b]An asterisk indicates that the experiment was performed by adding chemicals to the previous experiment. Cumulative amounts are given.
[c]The $LiAlCl_4$ was actually made by mixing LiCl and $AlCl_3$ such that there was a small excess of LiCl (0.66 mg LiCl per gram salt). This was neglected in the calculations.
[d]The mole fraction X_{LiAlCl_4} was calculated from the number of moles of $LiAlCl_4$ and $SOCl_2$ using a thionyl chloride density of 1.630 g cm^{-3} at 25°C.
[e]Obtained by calculation, using data from Ref. (5), see Appendix. At concentrations above 1.5*M*, the accuracy is low (extrapolation).

Measurements.—Conductivity measurements were done outside of the glove box, after allowing sufficient time to elapse for compounds to dissolve and temperature equilibrium to be established. Better than ± 0.2°C temperature control was obtained by placing the cells in a refrigerator (at −20°C), in a well-stirred ice water bath (at 0°C) and in a well-stirred paraffin-oil bath, thermostated at *ca.* 25°, 45°, and 70°C. Temperatures were measured with a 100 Ω Pt resistance thermometer to a precision better than 0.1°C. Finally, cell resistances (R) within a 0.03% relative precision were determined by means of a precision ac-Wheatstone bridge (10) using a 2 kHz and 0.2V amplitude signal. The results were largely independent of the applied frequency and voltage.

General considerations.—By definition the electrical conductance is the reciprocal of the resistance. The specific conductivity is reported as $\kappa = l/(R \cdot A)$, where l is length in cm and A is cross-sectional area in cm^2. In conductivity cells, the ratio l/A, the so-called cell constant was obtained by the calibration procedure (11).

The concentrations are given by mole fractions defined in the following way: $X_{LiAlCl_4} = n_{LiAlCl_4}/(n_{LiAlCl_4} + n_{SOCl_2})$ and $X'_{AlCl_3} = (n_{AlCl_3} + n_{LiAlCl_4})/(n_{AlCl_3} + 2n_{LiAlCl_4})$, where n is the number of moles of the index compound. X' is the internal mole fraction of the salts added, excluding the $SOCl_2$ solvent.

Results and Discussion

The conductivities for our approximately equimolar LiCl-$AlCl_3$ in thionyl chloride solutions are given in Table II and shown in Fig. 2. Since the experimental data points were not measured at a temperature of exactly −20°, 0°, 25°, 45°, or 70°C, small adjustments in κ were done to compensate for this. These corrections were performed by means of a smooth curve interpolation technique. It is clearly seen from Fig. 2 that (*i*) the conductivity of a given solution increases markedly with temperature and (*ii*) a maximum in conductivity *vs.* X_{LiAlCl_4} is found at each temperature. This maximum is shifted towards more concentrated solutions for higher temperatures. The occurrence of such a maximum is a well-established phenomenon in electrolytes (8, 12). A tentative explanation is given as follows.

In dilute solutions, the Li^+ ions move rather freely and carry most of the current. Hence, the more Li^+ present, the higher the conductivity. In concentrated solutions, some

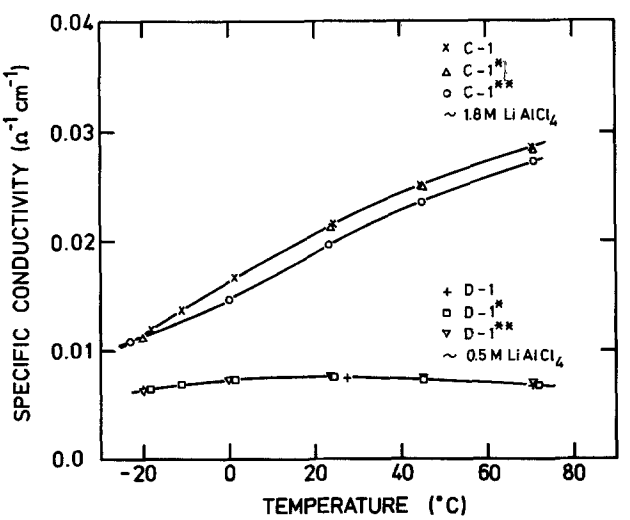

Fig. 3. Specific conductivity *vs.* temperature for 0.5*M* and 1.8*M* $LiAlCl_4$ solutions in $SOCl_2$, to which various amounts of $AlCl_3$ have been added. Experiment numbers refer to Table II and III.

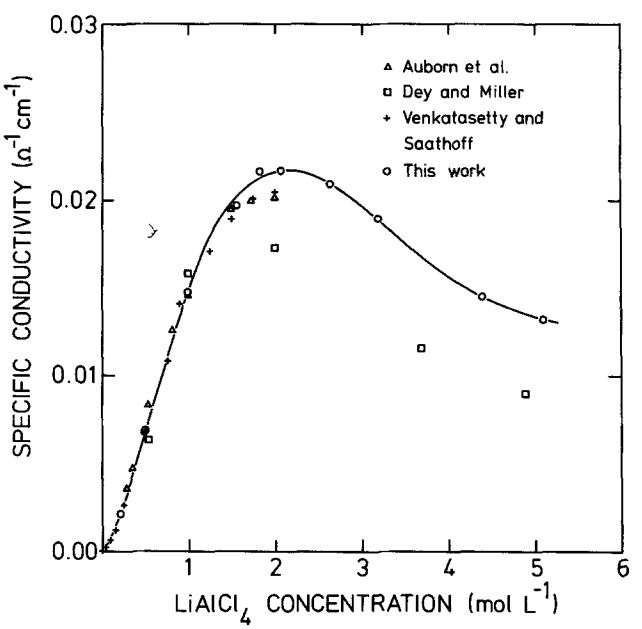

Fig. 4. Experimental conductivity of $LiAlCl_4$-$SOCl_2$ solutions at 25°C *vs.* molar concentration.

Table II. Specific conductivity of $LiAlCl_4$-$SOCl_2$ solutions[a]

Cell experiment	X_{LiAlCl_4}	Approximate concentration (25°C) mol/liter	Temp. (°C)	Conductivity $\kappa \cdot 10^3$ S cm^{-1}
B-3	0.0152	0.208	−18.7	2.38
			−1.05	2.408
			23.1	2.194
			45.6	1.884
			70.3	1.548
A-1	0.0354	0.485	−19.0	6.08
			0.0	6.98
			22.2	6.92
			47.0	6.59
			74.7	5.98
A-4	0.0361	0.495	−18.7	6.15
			−0.94	6.908
			23.1	7.097
			45.5	6.95
			70.8	6.32
B-1	0.0723	0.991	−19.0	10.42
			0.0	13.11
			22.2	14.58
			47.0	15.60
			74.7	15.96
B-1*	0.1136	1.556	−18.9	11.71
			0.0	15.53
			23.6	19.56
			44.4	22.16
			69.8	24.43
C-1	0.1338	1.83	−18.1	12.00
			−11.0	13.73
			1.35	16.61
			24.5	21.58
			44.6	25.04
			70.5	28.58
A-2	0.1520	2.08	−18.9	10.92
			0.0	15.69
			22.6	21.17
			45.2	25.95
			70.5	30.17
A-2*	0.1929	2.64	−19.4	8.82
			−0.46	14.06
			21.7	19.98
			21.8	20.18
			46.2	26.54
			44.0	26.19
			71.1	32.69
			70.7	32.59
B-2	0.2343	3.2	−19.4	6.87
			−0.46	11.58
			21.8	17.94
			46.2	25.20
			71.1	32.79
B-2*	0.3232	4.4	−18.9	3.81
			−0.15	7.57
			22.1	13.70
			45.5	21.68
			68.0	30.30
A-3	0.3735	5.1	−18.9	2.76
			−0.62	6.18
			21.1	12.04
			45.0	20.10
			68.0	29.63

[a]Symbols are explained in Table I.

limitations on lithium ion movement exist, and in higher concentrations the liquid is more viscous. These two effects lead to a conductivity maximum. We feel it is reasonable that the maximum in conductivity as a function of concentration occurs at a lower concentration at low temperatures, as observed. Another effect which may lead to a maximum in conductivity is a complex or adduct formation between Li^+, $AlCl_4^-$, and $SOCl_2$. Such complexes have been found in the $NaAlCl_4$-$POCl_3$ system (13).

The results given in Table II refer to approximately stoichiometric $LiAlCl_4$. Actually, the $LiAlCl_4$ used was slightly basic due to a slight excess of LiCl (see Table I).

To study the effect of the acidity ($X'_{AlCl_3} > 0.5$) on the conductivity, successive quantities of $AlCl_3$ were added in two of the experiments (C-1 and D-1, Table I). The resulting conductivities are given in Table III and depicted in Fig. 3.

When aluminum chloride was added to solutions containing a low concentration of $LiAlCl_4$ (*ca.* 0.5*M*), the conductivity remained unchanged or increased slightly. However, addition of aluminum chloride to about 1.8*M* $LiAlCl_4$ caused the conductivity to decrease. In view of the complexity of the problem (*i.e.*, acid/base reactions, adduct formation, complex formation, etc.) an explanation of this particular behavior cannot be given at the moment.

Our conductivities are compared to the results of the literature (2, 5, 8) as shown in Fig. 4. We can only compare results obtained at 25°C because we do not know our concentrations at other temperatures. Unfortunately, Dey and Miller (8) presented their results in a very restricted way so we are unable to discuss why they seem to have obtained somewhat lower conductivities than we have (Fig. 4). Otherwise, the agreement between our results and the literature is quite good. At higher concentrations, Venkatasetty and Szpak (6) give equations for the conductivity for solutions which also contain 0.5*M* dissolved SO_2 and 0.15*M* sulfur; see their Tables II, IV, and VI (6). Using their equa-

Table III. Specific conductivity of slightly acidic ($AlCl_3$-excessive) $LiAlCl_4$-$SOCl_2$ solutions[a]

Cell experiment	X_{LiAlCl_4}	X'_{AlCl_3}	Approximate concentration mol/liter	Temperature °C	Conductivity $\kappa \cdot 10^3$ S cm^{-1}
D-1	0.0375	0.5011	0.51	−19.8	6.44
				27.6	7.54
				70.6	6.78
D-1*	~0.0375	0.508	0.5	−18.2	6.51
				−11.0	6.94
				1.4	7.35
				24.5	7.59
				45.2	7.37
				72.1	6.82
D-1**	~0.0375	0.542	0.5	−19.9	6.43
				0.0	7.37
				23.7	7.74
				45.4	7.55
				70.9	7.05
C-1*	~0.0375	0.505	1.8	−20.1	11.08
				23.7	21.18
				45.3	24.90
				70.9	28.33
C-1**	~0.0375	0.539	1.8	−23.8	10.86
				0.0	14.66
				23.3	19.75
				44.9	23.58
				71.0	27.25

[a]Symbols are explained in Table I.

tions for $C_{LiCl} = C_{AlCl_3}$ at 20°C and neglecting the presence of SO_2 and sulfur yields good agreement with our work. At other temperatures, where the unknown contraction or expansion of solutions makes comparison more dubious, good consistency is still obtained (in general better than a few percent).

Expression for Calculating the Conductivity

The experimental data in Table II were used to derive an empirical expression from which the conductivity can be calculated as a function of composition ($X = X_{LiAlCl_4}$) and temperature (T, degrees Kelvin). The data were fitted to empirical power series like Eq. [1] by means of standard least squares regression methods (14). A-H are adjustable coefficients in Eq. [1]

$$\kappa = A + BT + CT^2 + DX + EX^2 + FX^3 + GTX + HTX^2 \quad [1]$$

These results were not particularly convincing and even the inclusion of terms, *e.g.*, in $X^{1/2}$, $X^{3/2}$, $TX^{1/2}$, and $X \ln X$ did not improve the fit very much. We then tried to fit $\ln \kappa$ to a power series. By trial and error we finally obtained the expression of Eq. [2], which successfully describes the measured data and has relatively few adjustable parameters (A-E). The values of the parameters obtained for Eq. [2] and other details are given in Table IV

$$\ln \kappa = A + B\frac{\ln X}{T} + C\frac{\sqrt{X}}{T} + D \ln X + E(T - 303.15)^2 \quad [2]$$

A three-dimensional representation of Eq. [2] is shown in Fig. 5. The maximum in conductivity and its shift with temperature can easily be seen.

At the present it is not possible to provide a detailed explanation for the behavior of the conductivity in the system studied here. Several chemical equilibria may be involved during changes in temperatures and compositions. Recent Raman spectroscopic work may help to better understand the situation (15).

Table IV. Analytical expression fitting the specific conductivity data in Table II better than $1.0 \cdot 10^{-3}$ S cm^{-1}[a,b]

$$\ln \kappa = A + B\frac{\ln X}{T} + C\frac{\sqrt{X}}{T} + D \ln X + E(T - 303.15)^2$$

$A = 5.734 \pm 0.1$
$B = -240.13 \pm 9.6$ (K)
$C = -3744.435 \pm 46$ (K)
$D = 3.286 \pm 0.05$
$E = (-7.033 \pm 0.84) \cdot 10^{-5}$ (K^{-2})

$X = X_{LiAlCl_4}$
T = absolute temperature

[a]The coefficient of determination (13), R^2, which is 1.0 for a perfect fit, is 0.99586.
[b]Standard deviation on $\ln \kappa$ is 0.05.

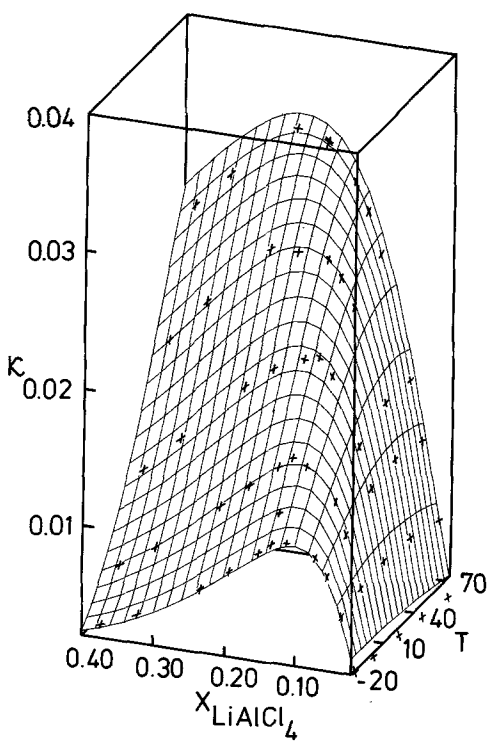

Fig. 5. Calculated conductivity of $LiAlCl_4$-$SOCl_2$ solutions. The X, T (in °C) positions of the experimental observations are indicated on the surface calculated from the polynomial expression of κ (Table IV), see also Fig. 2.

Acknowledgments

GN Batteries, Incorporated, (Hellesens) is thanked for help during the work. The Danish Ministry of Energy and the Danish Technical Research Council as well as Direktør

Table A-I. Concentration, density, and mole fraction of $LiAlCl_4$-$SOCl_2$ solutions at 25°C, based on the experiment of Venkatasetty and Saathoff (5)

Concentration (mol/liter)	Density (g/cm^3)	X_{LiAlCl_4}[a]
0.00249	1.6438	0.00018
0.00997	1.6443	0.00072
0.03046	1.6451	0.00220
0.04985	1.64599	0.00360
0.0997	1.64820	0.00722
0.200	1.6525	0.01450
0.35	1.65903	0.02540
0.50	1.66555	0.03633
0.65	1.67206	0.04729
0.75	1.6764	0.054395
0.90	1.68293	0.06561
1.00	1.68727	0.07296
1.50	1.7090	0.109895

[a]Calculated by iteration as explained in the text.

Ib Henriksens Fond are thanked for providing the financial basis of this work.

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Note added in proof: Recent measurements (16) agree well with our measurements also at high concentrations.

APPENDIX

To facilitate comparisons with the literature, data given by Venkatasetty and Saathoff (5) for the density of the $SOCl_2$ solution *vs.* the molar $LiAlCl_4$ concentration have been used to estimate approximate concentrations. The calculations were based on their data points (see Table A-I), using an iterative method. We assumed p grams of $LiAlCl_4$ per mole of $SOCl_2$. Thus, $p = C \cdot 175.732\,(118.9894 + p)/1000 \cdot \rho$, where C is the molar $LiAlCl_4$ concentration, ρ is the density, and the numbers shown are the molar masses of $LiAlCl_4$ and $SOCl_2$. From p values calculated iteratively, the molar fraction of $LiAlCl_4$ is easily obtained for each of the given concentrations. Then the C and ρ data were treated by regression *vs.* X_{LiAlCl_4} to give linear dependencies

$$(C \pm 0.0025) = (13.7007 \pm 0.0143) \cdot X_{LiAlCl_4} \quad (R^2 = 0.999987)$$

and

$$(\rho \pm 0.0001) = (0.594484 \pm 0.000934) \cdot X_{LiAlCl_4} + (1.64388 \pm 0.00004) \quad (R^2 = 0.99997)$$

These lines are valid in the range $0 < X_{LiAlCl_4} < 0.11$, $0 < C < 1.50$ mol/liter and $1.64 < \rho < 1.71$ g/cm^3 and at 25°C. At higher concentrations linear extrapolation cannot be done with confidence. Therefore the concentrations in Table II are shown with few digits.

It should be noted that the equation for the density does not extrapolate to the generally accepted room temperature value 1.629 g/cm^3 for $SOCl_2$ (17).

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A Mathematical Model of a Lithium/Thionyl Chloride Primary Cell

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ABSTRACT

A one-dimensional mathematical model for the lithium/thionyl chloride primary cell has been developed to investigate methods of improving its performance and safety. The model includes many of the components of a typical lithium/thionyl chloride cell such as the porous lithium chloride film which forms on the lithium anode surface. The governing equations are formulated from fundamental conservation laws using porous electrode theory and concentrated solution theory. The model is used to predict one-dimensional, time dependent profiles of concentration, porosity, current, and potential as well as cell temperature and voltage. When a certain discharge rate is required, the model can be used to determine the design criteria and operating variables which yield high cell capacities. Model predictions can be used to establish operational and design limits within which the thermal runaway problem, inherent in these cells, can be avoided.

The lithium/thionyl chloride ($Li/SOCl_2$) cell is an attractive primary energy source because of its high energy density (1, 2). However, researchers have observed that the $Li/SOCl_2$ cell is a serious safety hazard under certain conditions (2). High discharge rates and high temperatures promote thermal runaway which can result in the venting of toxic gases and explosion. A mathematical model of this battery has been developed to investigate the operational and design characteristics which can be adjusted to yield efficient, yet acceptably safe $Li/SOCl_2$ cells.

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Description of a $Li/SOCl_2$ Cell

The model describes the $Li/SOCl_2$ cell illustrated in Fig. 1. The four cell regions are the lithium chloride (LiCl) film which forms on the anode surface, the separator (usu-